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(54) **Process and compositions for compact detergents.**

(57) A high active granular detergent composition is prepared by making a base powder with a bulk density of at least 600 g/l and having less than 10% by weight of particles less than 150 microns and less than 10% by weight of particles greater than 1700 microns.

Additional ingredients are post-added comprising filler particles having a defined particle size range which further increases the bulk density of the finished product while maintaining good dispensing and dissolution properties.

**EP 0 578 871 A1**

FIELD OF THE INVENTION

The present invention relates to a process for making improved high bulk density detergent compositions which dissolve rapidly and dispense effectively, and the resulting compositions made by this process.

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BACKGROUND OF THE INVENTION

There is a trend amongst commercially available granular detergents towards higher bulk densities and towards granular detergent components which have a higher content of detergent active ingredients. Such detergents offer greater convenience to the consumer, and at the same time reduce the amount of packaging materials which will, ultimately, be disposed of.

Many of the prior art attempts to move in this direction have met with problems of poor solubility properties arising from low rate of dissolution or the formation of gels. A consequence of this in a typical washing process can be poor dispensing of the product, either from the dispensing drawer of a washing machine, or from a dosing device placed with the laundry inside the machine. This poor dispensing is often caused by gelling of particles which have high levels of surfactant upon contact with water. The gel prevents a proportion of the detergent powder from being solubilized in the wash water which reduces the effectiveness of the powder. Another adverse consequence arises even if the powder is well dispensed and dispersed in the washing water if it does not dissolve rapidly. The wash cycle has a limited duration during which the detergent can act upon the laundry. If the cleaning action is delayed because the powder is slow to dissolve, this, too, will limit the effectiveness of the powder.

The process engineer and formulator have frequently found that the need for good dispensing and the need for good dissolution rate have placed conflicting demands upon them. The solution has generally been to find a compromise which gives adequate dispensing and a adequate dispensing and adequate dissolution rate. For example, poor dispensing of high bulk density granular detergents is often associated with surfactant rich particles of low porosity, and having a small particle size (especially "fines"). However, increasing the average particle size reduces the rate of dissolution as well as imposing a limit on the bulk density that can then be achieved.

Many processes described in the prior art have disclosed methods of making denser particles from powders that have been made by the traditional spray drying process. EP-A- 220 024, published on April 29, 1987, describes a process of compacting spray dried powders in order to produce a high bulk density composition, which, it is claimed has good dissolving properties. It is suggested that the presence of silicate reduces the tendency to gel, however, it also points out that high levels of silicate cause problems of insoluble particles.

Another processing route is described in GB 2 166 452, published on May 8, 1986, this patent proposes a process for making a detergent composition with a high bulk density and good solubility properties. This process is based on agglomeration in a kneader forming pellets, followed by granulation to the required particle size distribution in, for example, a hammer mill.

Other processes in the prior art have sought to avoid the step of granulating pellets or compacting which is capital-intensive and expensive. One such method which has been described to further increase the bulk density of a spray dried composition is the post addition of fine particles of high density sodium sulphate. EP-A-219 328, published on April 22, 1992, describes the sulphate as filler particles, which, added at levels of from 20% to 35%, by weight of the finished composition, can increase the bulk density of a spray dried powder by at least 150 g/l. EP-A- 270 240, published on June 6, 1988, describes compositions suitable for spray drying which give a powder of low porosity (< 40%) and high bulk density in comparison with traditional spray dried powders. Post dosing of sulphate filler particles to further increase bulk density is again proposed. However, the sulphate particles serve only to increase the bulk density, but do not contribute to the washing process itself.

Japanese patent number 83/213099, published on December 10, 1983, also describes the addition of fine filler particles to a spray dried base powder. In this instance the benefits are directed towards improving the anti-caking properties of the finished composition.

It is known that high active particles can be made by various agglomeration processes, such as that described in EP-A-340 013. This application describes a process and composition for high bulk density powders. However, the highest bulk densities of the agglomerated base powders are achieved when the level of fines is higher. When this is the case, post addition of dry powders does not increase the bulk density any further and may indeed decrease it. Furthermore if the fines contain surfactant, the tendency for gelling and poor dispensing may be increased.

It is the aim of this invention to provide a detergent composition which has a high activity of detergent active ingredients, as well as a high level of other ingredients which are active in the washing process (such as builder etc.), which also has properties of rapidly and completely dissolving in water without forming a gel, and which has a high bulk density. This has been achieved by firstly removing the surfactant containing fines from an agglomerated base powder, and secondly post adding rapidly-dissolving, non-gelling particles of a defined particle size in order to ensure a wide particle size distribution of the finished product which contributes to a high bulk density of the finished product.

It has been found that either particles with an average particle size of less than 150 microns which do not promote gel formation, and/or, particles greater than 1700 microns which are still rapidly dissolving, are particularly suitable for post addition in process of the present invention.

In a preferred embodiment of the invention, the post-dosed materials are either citrates or inorganic salts, chosen because they are quickly soluble with forming gels. Most preferred are post-dosed materials which are functional in the washing process, especially builders such as citrates, carbonates, bicarbonates and non-hygroscopic forms of silicates.

#### SUMMARY OF THE INVENTION

The invention describes a process for the preparation of a compact granular detergent composition comprising one or more detergent active ingredients and comprising the steps of:

- i) making a base powder in the form of a free-flowing powder having a bulk density of at least 600g/l and having less than 10% by weight of particles less than 150 microns and less than 10% by weight of particles greater than 1700 microns.
- ii) post-addition of filler particles between 5% and 20% by weight of the finished product whereby at least 20% by weight of the filler particles is either less than 150 microns, or greater than 1180 microns.
- iii) optionally, post-addition and/or spray-on of additional ingredients.

#### DETAILED DESCRIPTION OF THE INVENTION

Granular detergent particles (referred to as a base powder) made by any suitable process, are generally separated according to particle size. Fines are removed, for example in a cyclone, and oversize particles are removed, for example on a sieve.

For the purposes of the present invention a base powder which has greater than 90% by weight which does not pass through a Tyler sieve mesh 100 (aperture size = 150 microns), and also greater than 90% by weight passing through a Tyler sieve mesh 10 (aperture size = 1700 microns) is suitable for further processing.

During subsequent processing at least one additional powder is mixed with the base powder. For the purposes of the present document, this powder (or powders) is referred to as a "filler", because it is an essential feature of the invention that the void space between particles is (at least partially) filled. However, it must be realised that the filler particles of this invention may also be active in the wash process, for example as builders or pH buffers. The essential feature of the filler is that it should be rapidly soluble in water with no tendency to form a gel.

#### Suitable "Filler" Particles

Suitable filler particles are chosen against criteria of particle size, solubility characteristics and functional properties in the washing process.

Particle size is chosen so that bulk density of the total composition is increased. This is achieved by adding fine filler particles (at least 20%, preferably at least 40%, by weight of the filler particles passing through a Tyler sieve mesh 100) which occupy the voids between the base particles, and/or by adding large filler particles (at least 20%, preferably at least 40%, by weight of the filler particles not passing through a Tyler sieve mesh 14), which causes base particles to occupy the voids between the filler particles.

Generally, it is preferred that the filler particles have an average particle size of not less than 50 microns. Filler particles below this average particle size tend to coat the surface of the base granules rather than fill the voids between them.

Preferred filler particles will also have a function in the washing process. Examples of this include builders, pH buffers and corrosion inhibitors.

Solubility of the filler particles should be such that they do not form a gel upon contact with water, but they do dissolve rapidly into aqueous solution. Clearly, this criterion is, itself, influenced by particle size and

detergent properties mentioned above. The rate of dissolution required will depend upon what function the filler particle plays in the washing process and whether that function must take effect early in the wash cycle (ie very rapid rate of dissolving required), or whether the function can be fulfilled equally well later in the wash cycle (ie a slower rate of dissolving is acceptable). The rate of dissolving will, in turn, be influenced by the particle size distribution of the filler particles chosen (larger particles dissolving slower than small ones).

Preferred filler particles for use in this invention include sodium, potassium and magnesium salts of citrates, sulphates, carbonates, bicarbonates and silicates (silicates in their non-hygroscopic forms). Especially preferred are sodium citrate and layered forms of sodium silicate, both of which serve as builders in the finished composition, as well as sodium bicarbonates. Layered silicates such as those marketed by Hoechst under the registered trade name SKS-6 is one example of a suitable filler material.

In addition to the filler particles described hereinabove, other ingredients may be added to complete a finished detergent composition by any means familiar to the man skilled in the art of detergents processing. Examples include dry addition of additional dry powders and/or spraying on of liquids.

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#### Base Powder Processing

Any process which gives a base powder with a bulk density of at least 600g/l is suitable for use in this invention. These bulk densities are typical of powders made by various densification processes, or made by dry mixing powders and agglomerating with liquid binders (including surfactants and surfactant pastes).

A particularly preferred process is by way of granulating a high active paste comprising a salt or salts of detergent active materials (surfactant) with an effective weight of dry-mixed powder. The paste and the powder are treated in a high speed mixer, in which a rotating shaft carrying cutting and mixing tools is rotated. This serves to rapidly disperse the high active paste preventing local accumulations which could cause lumps to form. In subsequent processing steps the paste/powder mixture is granulated to form non-sticky, free-flowing powder.

#### The Pastes

One or various aqueous pastes of the salts of anionic surfactants is preferred for use in the present invention, preferably the sodium salt of the anionic surfactant. In a preferred embodiment, the anionic surfactant is preferably as concentrated as possible, (that is, with the lowest possible moisture content possible that allows it to flow in the manner of a liquid) so that it can be pumped at temperatures at which it remains stable. While granulation using various pure or mixed surfactants is known, for the present invention to be of practical use in industry and to result in particles of adequate physical properties to be incorporated into granular detergents, an anionic surfactant must be part of the paste in a concentration of above 10%, preferably from 10-95%, more preferably from 20-95%, and most preferably from 40%-95%.

It is preferred that the moisture in the surfactant aqueous paste is as low as possible, while maintaining paste fluidity, since low moisture leads to a higher concentration of the surfactant in the finished particle. Preferably the paste contains between 5 and 40% water, more preferably between 5 and 30% water and most preferably between 5 and 20% water. A highly attractive mode of operation for lowering the moisture of the paste prior to entering the agglomerator without problems with very high viscosities is the installation, in line, of an atmospheric or a vacuum flash drier whose outlet is connected to the agglomerator.

It is preferable to use high active surfactant pastes to minimize the total water level in the system during mixing, granulating and drying. Lower water levels allow for: (1) a higher active surfactant to builder ratio, e.g., 1:1; (2) higher levels of other liquids in the formula without causing dough or granular stickiness; (3) less cooling, due to higher allowable granulation temperatures; and (4) less granular drying to meet final moisture limits.

Two important parameters of the surfactant pastes which can affect the mixing and granulation step are the paste temperature and viscosity. Viscosity is a function, among others, of concentration and temperature, with a range in this application from about 5,000 mPas to 10,000,000 mPas. Preferably, the viscosity of the paste entering the system is from about 20,000 to about 100,000 mPas. and more preferably from about 30,000 to about 70,000 mPas. The viscosity of the paste of this invention is measured at a temperature of 70 °C.

The paste can be introduced into the mixer at an initial temperature between its softening point (generally in the range of 40-60 °C) and its degradation point (depending on the chemical nature of the paste, e.g. alkyl sulphate pastes tend to degrade above 75-85 °C). High temperatures reduce viscosity simplifying the pumping of the paste but result in lower active agglomerates. The use of in-line moisture

reduction steps (e.g. flash drying), however, require the use of higher temperatures (above 100°C). In the present invention, the activity of the agglomerates is maintained high due to the elimination of moisture.

The introduction of the paste into the mixer can be done in many ways, from simply pouring to high pressure pumping through small holes at the end of the pipe, before the entrance to the mixer. While all these ways are viable to manufacture agglomerates with good physical properties, it has been found that in a preferred embodiment of the present invention the extrusion of the paste results in a better distribution in the mixer which improves the yield of particles with the desired size. The use of high pumping pressures prior to the entrance in the mixer results in an increased activity in the final agglomerates. By combining both effects, and introducing the paste through holes (extrusion) small enough to allow the desired flow rate but that keep the pumping pressure to a maximum feasible in the system, highly advantageous results are achieved.

#### High Active Surfactant Paste

The activity of the aqueous surfactant paste is at least 30% and can go up to about 95%; preferred activities are : 50-80% and 65-75%. The balance of the paste is primarily water but can include a processing aid such as a nonionic surfactant. At the higher active concentrations, little or no builder is required for cold granulation of the paste. The resultant concentrated surfactant granules can be added to dry builders or powders or used in conventional agglomeration operations. The aqueous surfactant paste contains an organic surfactant selected from the group consisting of anionic, zwitterionic, ampholytic and cationic surfactants, and mixtures thereof. Anionic surfactants are preferred. Nonionic surfactants are used as secondary surfactants or processing aids and are not included herein as an "active" surfactant. Surfactants useful herein are listed in U.S. Pat. No. 3,664,961, Norris, issued May 23, 1972, and in U.S. Pat. No. 3,919,678, Laughlin et al., issued Dec. 30, 1975. Useful cationic surfactants also include those described in U.S. Pat. No. 4,222,905, Cockrell, issued Sept. 16, 1980, and in U.S. Pat. 4,239,659, Murphy, issued Dec. 16, 1980. However, cationic surfactants are generally less compatible with the aluminosilicate materials herein, and thus are preferably used at low levels, if at all, in the present compositions. The following are representative examples of surfactants useful in the present compositions.

Water-soluble salts of the higher fatty acids, i.e., "soaps", are useful anionic surfactants in the compositions herein. This includes alkali metal soaps such as the sodium, potassium, ammonium, and alkylammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

Useful anionic surfactants also include the water-soluble salts, preferably the alkali metal, ammonium and alkylammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C<sub>8</sub>-C<sub>18</sub> carbonatoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the sodium and potassium alkyl benzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight or branched chain configuration, e.g., those of the type described in U.S. Pat. Nos. 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkyl benzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 13, abbreviated as C<sub>11</sub>-C<sub>13</sub> LAS.

Other anionic surfactants herein are the sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates containing from about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl groups contain from about 8 to about 12 carbon atoms; and sodium or potassium salts of alkyl ethylene oxide ether sulfates containing from about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl group contains from about 10 to about 20 carbon atoms.

Other useful anionic surfactants herein include the water-soluble salts of esters of alpha-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; alkyl ether sulfates containing from about 10 to 20 carbon atoms in the alkyl group and from about 1 to 30 moles of ethylene oxide; watersoluble salts of olefin sulfonates containing from about 12 to 24 carbon atoms; and

beta-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to about 20 carbon atoms in the alkane moiety. Although the acid salts are typically discussed and used, the acid neutralization can be performed as part of the fine dispersion mixing step.

The preferred anionic surfactant pastes are mixtures of linear or branched alkylbenzene sulfonates having an alkyl of 10-16 carbon atoms and alkyl sulfates having an alkyl of 10-18 carbon atoms. These pastes are usually produced by reacting a liquid organic material with sulfur trioxide to produce a sulfonic or sulfuric acid and then neutralizing the acid to produce a salt of that acid. The salt is the surfactant paste discussed throughout this document. The sodium salt is preferred due to end performance benefits and cost of NaOH vs. other neutralizing agents, but is not required as other agents such as KOH may be used.

Water-soluble nonionic surfactants are also useful as secondary surfactant in the compositions of the invention. Indeed, preferred processes use anionic/nonionic blends. A particularly preferred paste comprises a blend of nonionic and anionic surfactants having a ratio of from about 0.01:1 to about 1:1, more preferably about 0.05:1. Nonionics can be used up to an equal amount of the primary organic surfactant. Such nonionic materials include compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyalkylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Suitable nonionic surfactants include the polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 16 carbon atoms, in either a straight chain or branched chain configuration, with from about 4 to 25 moles of ethylene oxide per mole of alkyl phenol.

Preferred nonionics are the water-soluble condensation products of aliphatic alcohols containing from 8 to 22 carbon atoms, in either straight chain or branched configuration, with from 4 to 25 moles of ethylene oxide per mole of alcohol. Particularly preferred are the condensation products of alcohols having an alkyl group containing from about 9 to 15 carbon atoms with from about 4 to 25 moles of ethylene oxide per mole of alcohol; and condensation products of propylene glycol with ethylene oxide.

Semi-polar nonionic surfactants include water-soluble amine oxides containing one alkyl moiety of from about 10 to 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of about 10 to 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to 3 carbon atoms.

Ampholytic surfactants include derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic moiety can be either straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and at least one aliphatic substituent contains an anionic water-solubilizing group.

Zwitterionic surfactants include derivatives of aliphatic quaternary ammonium phosphonium, and sulfonium compounds in which one of the aliphatic substituents contains from about 8 to 18 carbon atoms.

Particularly preferred surfactants herein include linear alkylbenzene sulfonates containing from about 11 to 14 carbon atoms in the alkyl group; tallow alkyl sulfates; coconutalkyl glyceryl ether sulfonates; alkyl ether sulfates wherein the alkyl moiety contains from about 14 to 18 carbon atoms and wherein the average degree of ethoxylation is from about 1 to 4; olefin or paraffin sulfonates containing from about 14 to 16 carbon atoms; alkyldimethylamine oxides wherein the alkyl group contains from about 11 to 16 carbon atoms; alkyldimethylammonio propane sulfonates and alkyldimethylammonio hydroxy propane sulfonates wherein the alkyl group contains from about 14 to 18 carbon atoms; soaps of higher fatty acids containing from about 12 to 18 carbon atoms; condensation products of C9-C15 alcohols with from about 3 to 8 moles of ethylene oxide, and mixtures thereof.

Useful cationic surfactants include water-soluble quaternary ammonium compounds of the form  $R_4R_5R_6R_7N^+X^-$ , wherein  $R_4$  is alkyl having from 10 to 20, preferably from 12-18 carbon atoms, and  $R_5$ ,  $R_6$  and  $R_7$  are each  $C_1$  to  $C_7$  alkyl preferably methyl;  $X^-$  is an anion, e.g. chloride. Examples of such trimethyl ammonium compounds include  $C_{12-14}$  alkyl trimethyl ammonium chloride and cocalkyl trimethyl ammonium methosulfate.

Specific preferred surfactants for use herein include: sodium linear  $C_{11}$ - $C_{13}$  alkylbenzene sulfonate; alpha-olefin sulphonates; triethanolammonium  $C_{11}$ - $C_{13}$  alkylbenzene sulfonate; alkyl sulfates, (tallow, coconut, palm, synthetic origins, e.g.  $C_{45}$ , etc.); sodium alkyl sulfates; methyl ester sulphonate; sodium coconut alkyl glyceryl ether sulfonate; the sodium salt of a sulfated condensation product of a tallow alcohol with

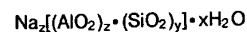
about 4 moles of ethylene oxide; the condensation product of a coconut fatty alcohol with about 6 moles of ethylene oxide; the condensation product of tallow fatty alcohol with about 11 moles of ethylene oxide; the condensation of a fatty alcohol containing from about 14 to about 15 carbon atoms with about 7 moles of ethylene oxide; the condensation product of a C<sub>12</sub>-C<sub>13</sub> fatty alcohol with about 3 moles of ethylene oxide; 3-(N,N-dimethyl-N-coconutalkylammonio)-2-hydroxypropane-1-sulfonate; 3-(N,N-dimethyl-N-coconutalkylammonio)-propane-1-sulfonate; 6-(N-dodecylbenzyl-N,N-dimethylammonio) hexanoate; dodecyldimethylamine oxide; coconutalkyldimethylamine oxide; and the water-soluble sodium and potassium salts of coconut and tallow fatty acids.

(As used herein, the term "surfactant" means non-nonionic surfactants, unless otherwise specified. The ratio of the surfactant active (excluding the nonionic(s)) to dry detergent builder or powder ranges from 0.005:1 to 19:1, preferably from 0.05:1 to 10:1, and more preferably from 0.1:1 to 5:1. Even more preferred said surfactant active to builder ratios are 0.15:1 to 1:1; and 0.2:1 to 0.5:1).

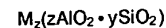
#### Builders and Powders

Any compatible builder or combination of builders and/or other powders can be used in the process and compositions of the present invention.

The detergent compositions herein can contain crystalline aluminosilicate ion exchange material of the formula



wherein z and y are at least about 6, the molar ratio of z to y is from about 1.0 to about 0.4 and z is from about 10 to about 264. Amorphous hydrated aluminosilicate materials useful herein have the empirical formula



wherein M is sodium, potassium, ammonium or substituted ammonium, z is from about 0.5 to about 2 and y is 1, said material having a magnesium ion exchange capacity of at least about 50 milligram equivalents of CaCO<sub>3</sub> hardness per gram of anhydrous aluminosilicate. Hydrated sodium Zeolite A with a particle size of from about 1 to 10 microns is preferred.

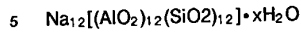
The aluminosilicate ion exchange builder materials herein are in hydrated form and contain from about 10% to about 28% of water by weight if crystalline, and potentially even higher amounts of water if amorphous. Highly preferred crystalline aluminosilicate ion exchange materials contain from about 18% to about 22% water in their crystal matrix. The crystalline aluminosilicate ion exchange materials are further characterized by a particle size diameter of from about 0.1 micron to about 10 microns. Amorphous materials are often smaller, e.g., down to less than about 0.01 micron. Preferred ion exchange materials have a particle size diameter of from about 0.2 micron to about 4 microns. The term "particle size diameter" herein represents the average particle size diameter by weight of a given ion exchange material as determined by conventional analytical techniques such as, for example, microscopic determination utilizing a scanning electron microscope. The crystalline aluminosilicate ion exchange materials herein are usually further characterized by their calcium ion exchange capacity, which is at least about 200 mg equivalent of CaCO<sub>3</sub> water hardness/g of aluminosilicate, calculated on an anhydrous basis, and which generally is in the range of from about 300 mg eq./g to about 352 mg eq./g. The aluminosilicate ion exchange materials herein are still further characterized by their calcium ion exchange rate which is at least about 2 grains Ca<sup>++</sup>/gallon/minute/gram/gallon of aluminosilicate (anhydrous basis), and generally lies within the range of from about 2 grains/gallon/minute/gram/gallon to about 6 grains/gallon/minute/gram/gallon, based on calcium ion hardness. Optimum aluminosilicate for builder purposes exhibit a calcium ion exchange rate of at least about 4 grains/gallon/minute/gram/gallon.

The amorphous aluminosilicate ion exchange materials usually have a Mg<sup>++</sup> exchange of at least about 50 mg eq. CaCO<sub>3</sub>/g (12 mg Mg<sup>++</sup>/g) and a Mg<sup>++</sup> exchange rate of at least about 1 grain/gallon/minute/gram/gallon. Amorphous materials do not exhibit an observable diffraction pattern when examined by Cu radiation (1.54 Angstrom Units).

Aluminosilicate ion exchange materials useful in the practice of this invention are commercially available. The aluminosilicates useful in this invention can be crystalline or amorphous in structure and can be naturally occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is discussed in U.S. Pat. No. 3,985,669, Krummel et al., issued Oct. 12, 1976,



incorporated herein by reference. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite B, and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula



wherein x is from about 20 to about 30, especially about 27 and has a particle size generally less than about 5 microns.

The granular detergents of the present invention can contain neutral or alkaline salts which have a pH in solution of seven or greater, and can be either organic or inorganic in nature. The builder salt assists in providing the desired density and bulk to the detergent granules herein. While some of the salts are inert, many of them also function as detergency builder materials in the laundering solution.

Examples of neutral water-soluble salts include the alkali metal, ammonium or substituted ammonium chlorides, fluorides and sulfates. The alkali metal, and especially sodium, salts of the above are preferred. Sodium sulfate is typically used in detergent granules and is a particularly preferred salt. Citric acid and, in general, any other organic or inorganic acid may be incorporated into the granular detergents of the present invention as long as it is chemically compatible with the rest of the agglomerate composition.

Other useful water-soluble salts include the compounds commonly known as detergent builder materials. Builders are generally selected from the various water-soluble, alkali metal, ammonium or substituted ammonium phosphates, polyphosphates, phosphonates, polyphosphonates, carbonates, silicates, borates, and polyhydroxysulfonates. Preferred are the alkali metal, especially sodium, salts of the above.

Specific examples of inorganic phosphate builders are sodium and potassium tripolyphosphate, pyrophosphate, polymeric metaphosphate having a degree of polymerization of from about 6 to 21, and orthophosphate. Examples of polyphosphonate builders are the sodium and potassium salts of ethylene diphosphonic acid, the sodium and potassium salts of ethane 1-hydroxy-1,1-diphosphonic acid and the sodium and potassium salts of ethane, 1,1,2-triphosphonic acid. Other phosphorus builder compounds are disclosed in U.S. Pat. Nos. 3,159,581; 3,213,030; 3,422,021; 3,422,137; 3,400,176 and 3,400,148, incorporated herein by reference.

Examples of nonphosphorus, inorganic builders are sodium and potassium carbonate, bicarbonate, sesquicarbonate, tetraborate decahydrate, and silicate having a molar ratio of  $\text{SiO}_2$  to alkali metal oxide of from about 0.5 to about 4.0, preferably from about 1.0 to about 2.4. The compositions made by the process of the present invention does not require excess carbonate for processing, and preferably does not contain over 2% finely divided calcium carbonate as disclosed in U.S. Pat. No. 4,196,093, Clarke et al., issued Apr. 1, 1980, and is preferably free of the latter.

As mentioned above powders normally used in detergents such as zeolite, carbonate, silica, silicate, citrate, phosphate, perborate, etc. and process acids such as starch, can be used in preferred embodiments of the present invention.

#### Powder stream

Although the preferred embodiment of the process of the present invention involves introduction of the anionic surfactant in via pastes as described above, it is possible to have a certain amount via the powder stream, for example in the form of blown powder. In these embodiments, it is necessary that the stickiness and moisture of the powder stream be kept at low levels, thus preventing increased "loading" of the anionic surfactant and, thus, the production of agglomerates with too high of a concentration of surfactant. The liquid stream of a preferred agglomeration process can also be used to introduce other surfactants and/or polymers. This can be done by premixing the surfactant into one liquid stream or, alternatively by introducing various streams in the agglomerator. These two process embodiments may produce differences in the properties of the finished particles (dispensing, gelling, rate of dissolution, etc.), particularly, if mixed surfactants are allowed to form prior to particle formation. These differences can then be exploited to the advantage of the intended application for each preferred process.

It has also been observed that by using the presently described technology, it has been possible to incorporate higher levels of certain chemicals (e.g. nonionic, citric acid) in the final formula than via any other known processing route without detrimental effects to some key properties of the matrix (caking, compression, etc.).

The Fine Dispersion Mixing and Granulation

The term "fine dispersion mixing and/or granulation," as used herein, means mixing and/or granulation of the mixture in a fine dispersion mixer at a blade tip speed of from about 5m/sec. to about 50 m/sec., unless otherwise specified. The total residence time of the mixing and granulation process is preferably in the order of from 0.1 to 10 minutes, more preferably 0.1-5 and most preferably 0.2-4 minutes. The more preferred mixing and granulation tip speeds are about 10-45 m/sec. and about 15-40 m/sec.

Any apparatus, plants or units suitable for the processing of surfactants can be used for carrying out the process according to the invention. Suitable apparatus includes, for example, falling film sulphonating reactors, digestion tanks, esterification reactors, etc. For mixing/agglomeration any of a number of mixers/agglomerators can be used. In one preferred embodiment, the process of the invention is continuously carried out. Especially preferred are mixers of the Fukae<sup>R</sup> FS-G series manufactured by Fukae Powtech Kogyo Co., Japan; this apparatus is essentially in the form of a bowl-shaped vessel accessible via a top port, provided near its base with a stirrer having a substantially vertical axis, and a cutter positioned on a side wall. The stirrer and cutter may be operated independently of one another and at separately variable speeds. The vessel can be fitted with a cooling jacket or, if necessary, a cryogenic unit.

Other similar mixers found to be suitable for use in the process of the invention include Diosna<sup>R</sup> V series ex Dierks & Söhne, Germany; and the Pharma Matrix<sup>R</sup> ex T K Fielder Ltd., England. Other mixers believed to be suitable for use in the process of the invention are the Fuji<sup>R</sup> VG-C series ex Fuji Sangyo Co., Japan; and the Roto<sup>R</sup> ex Zanchetta & Co srl, Italy.

Other preferred suitable equipment can include Eirich<sup>R</sup>, series RV, manufactured by Gustav Eirich Hardheim, Germany; Lödige<sup>R</sup>, series FM for batch mixing, series CB and series KM for continuous mixing/agglomeration, manufactured by Lödige Maschinenbau GmbH, Paderborn Germany; Drais<sup>R</sup> T160 series, manufactured by Drais Werke GmbH, Mannheim Germany; and Winkworth<sup>R</sup> RT 25 series, manufactured by Winkworth Machinery Ltd., Berkshire, England.

The Littleford Mixer, Model #FM-130-D-12, with internal chopping blades and the Cuisinart Food Processor, Model #DCX-Plus, with 7.75 inch (19.7 cm) blades are two examples of suitable mixers. Any other mixer with fine dispersion mixing and granulation capability and having a residence time in the order of 0.1 to 10 minutes can be used. The "turbine-type" impeller mixer, having several blades on an axis of rotation, is preferred. The invention can be practiced as a batch or a continuous process.

Operating Temperatures

Preferred operating temperatures should also be as low as possible since this leads to a higher surfactant concentration in the finished particle. Preferably the temperature during the agglomeration is less than 80 °C, more preferably between 0 ° and 70 °C, even more preferably between 10 and 60 °C and most preferably between 20 and 50 °C. Lower operating temperatures useful in the process of the present invention may be achieved by a variety of methods known in the art such as nitrogen cooling, cool water jacketing of the equipment, addition of solid CO<sub>2</sub>, and the like; with a preferred method being solid CO<sub>2</sub>, and the most preferred method being nitrogen cooling.

A highly attractive option in a preferred embodiment of the present invention to further increase the concentration of surfactant in the final particle, is accomplished by the addition to a liquid stream containing the anionic surfactant and/or other surfactant, of other elements that result in increases in viscosity and/or melting point and/or decrease the stickiness of the paste. In a preferred embodiment of the process of the present invention the addition of these elements can be done in line as the paste is pumped into the agglomerator. Example of these elements can be various powders, such as those described in more detail hereinabove.

Drying

The desired moisture content of the free flowing granules of this invention can be adjusted to levels adequate for the intended application by drying in conventional powder drying equipment such as fluid bed dryers. If a hot air fluid bed dryer is used, care must be exercised to avoid degradation of heat sensitive components of the granules. It is also advantageous to have a cooling step prior to large scale storage. This step can also be done in a conventional fluid bed operated with cool air. The drying/cooling of the agglomerates can also be done in any other equipment suitable for powder drying such as rotary dryers, etc.

For detergent applications, the final moisture of the agglomerates needs to be maintained below levels at which the agglomerates can be stored and transported in bulk. The exact moisture level depends on the composition of the agglomerate but is typically achieved at levels of 1-8% free water (i.e. water not associated to any crystalline species in the agglomerate) and most typically at 1-4%.

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#### Final Base Powder Composition

Granules made by the process described hereinabove are of high density, and suitable for use in detergent compositions of the present invention. A preferred composition of the base powder for incorporation into granular detergents has a high surfactant concentration. By increasing the concentration of surfactant, the particles/agglomerates made by the present invention are more suitable for a variety of different formulations. These high surfactants containing particle agglomerates require fewer finishing techniques to reach the final agglomerates, thus freeing up large amounts of processing aids (inorganic powders, etc.) that can be used in other processing steps of the overall detergent manufacturing process (spray drying, dusting off, etc).

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The granules made according to the present invention are large, low dust and free flowing, and preferably have a bulk density of from about 600 to about 1000 g/l, more preferably from about 600 to about 800 g/l.

#### Polymers

Also useful in detergent compositions, are various organic polymers, some of which also may function as builders to improve detergency. Included among such polymers may be mentioned sodium carboxy-lower alkyl celluloses, sodium lower alkyl celluloses and sodium hydroxy-lower alkyl celluloses, such as sodium carboxymethyl cellulose, sodium methyl cellulose and sodium hydroxypropyl cellulose, polyvinyl alcohols (which often also include some polyvinyl acetate), polyacrylamides, polyacrylates and various copolymers, such as those of maleic and acrylic acids. Molecular weights for such polymers vary widely but most are within the range of 2,000 to 100,000.

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Polymeric polycarboxyate builders are set forth in U.S. Patent 3,308,067, Diehl, issued March 7, 1967.

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Such materials include the water-soluble salts of homo-and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylenemalononic acid.

#### Optionals

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Other ingredients commonly used in detergent compositions can be included in the compositions of the present invention. These include flow aids, color speckles, bleaching agents and bleach activators, suds boosters or suds suppressors, antitarnish and anticorrosion agents, soil suspending agents, soil release agents, dyes, fillers, optical brighteners, germicides, pH adjusting agents, nonbuilder alkalinity sources, hydrotropes, enzymes, enzyme-stabilizing agents, chelating agents and perfumes.

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Optical brighteners may be incorporated either directly in the agglomerates herein by way of the powder stream into the agglomerating unit, or in the finished composition by way of a spray-dried slurry, or via both of these routes.

Particulate suds suppressors may also be incorporated either directly in the agglomerates herein by way of the powder stream into the agglomerating unit, or in the finished composition by dry adding. Preferably the suds suppressing activity of these particles is based on fatty acids or silicones.

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#### Finished Compositions

Preferred compositions which can be made by the present invention, which are suitable for domestic laundry use are free-flowing granular detergents having a bulk density greater than 650 g/l and comprising

- i) from 5% to 25% by weight of anionic surfactant
- ii) from 5% to 30% by weight of aluminosilicate builder
- iii) from 5% to 20% by weight of filler particles comprising sodium, potassium or magnesium salts of citrates, sulphates, carbonates, bicarbonates or silicates, or a mixture thereof

characterised in that at least 40% by weight of the filler particles is either less than 150 microns, or greater than 1180 microns.

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Especially preferred is a composition in which the filler particles are either sodium citrate, or layered sodium silicate, or sodium bicarbonate, or a mixture of these.

The finished compositions may comprise a spray-dried component. However, in order to realise the benefits of bulk density and dispensing characteristics of the present invention, it is preferred that the finished product composition comprises less than 30% by weight of a spray dried component. Furthermore, where a spray dried component is included in the finished composition, it should preferably contain less than 10% by weight of anionic surfactant, preferably less than 4% by weight, most preferably any spray dried component should be surfactant free.

Improved dispensing and dissolution properties will normally be found when at least 80% by weight of the total amount of anionic surfactant present in the composition is in the fraction that passes through a Tyler sieve mesh 14, but does not pass through a Tyler Sieve mesh 65.

Further examples of typical compositions and methods for preparing them are given below:

### Examples

A base powder is prepared in the form of agglomerates using a batch Loedige FM (Trade Mark) as the mixer/granulator. The agglomerates were made by placing a mixture of powders into the mixer/granulator consisting of:

Zeolite A	23.8 kg
Sodium Carbonate	4.8 kg
Optical brightener	0.4 kg
MgSO <sub>4</sub>	1.0 kg

With the mixer/granulator operating, 3.6 kg of a solution 25% aqueous solution of phosphonate was added to the powder mixture. Immediately after, 19.1 kg of a high active anionic surfactant paste at 50 °C was poured into the mixer/granulator.

The high active surfactant paste had a total anionic surfactant activity of 76% and a water content of 20%. The surfactant in the paste consisted of a mixture of C14-15 alkyl sulphate (AS) and C13-15 alkyl ether sulphate with an average of 3 moles of ethylene oxide (AE3S), in the weight ratio of AS:AE3S of 80:20.

Granulation of the powders, liquid and paste occurred within 30 seconds of the addition of the paste. The agglomerates made were then dried in a fluid bed with an inlet air temperature of 90 °C until they reach an equilibrium relative humidity at 20 °C of 10-15%. The resulting agglomerates are referred to as the base powder.

40kg of this base powder was sieved through a Tyler sieve mesh 10 to remove the coarse fraction (>1700 microns), and on a Tyler sieve mesh 65 in order to remove the fines (<212 microns). The remaining fraction was then used to prepare a detergent composition containing:

Base powder (after sieving)	32 kg
Acrylic-maleic copolymer (granular)	2.4kg
Layered silicate (granular)	15.1 kg
Perborate monohydrate	17 kg
Bleach Activator (agglomerated)	7.3 kg
Suds suppressor (agglomerated)	2.0 kg
Soil Release Polymer (granular)	0.2 kg
Dobanol 25E3 (Trade mark, Shell)	5.7 kg
Perfume and enzymes	2.7 kg
Zeolite A (powder)	3.6 kg

The composition was made by mixing all of the dry components (except the zeolite) and evenly distributing the Dobanol and perfume onto the mixture by spraying. Then the zeolite A powder was added and allowed to mix for 3 minutes. Finally the batch was split into two equal portions and mixed with filler particles (in this example, the filler particles were sodium carbonate).

Half of the batch (44kg) was mixed with 6 kg ground carbonate with an average particle size of 175 microns. For comparison, the other half of the batch was mixed with 6 kg of commercially available granular carbonate, having a bulk density of 1050 g/l and an average particle size of about 400 microns.

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The particle size distributions (expressed cumulatively in weight %) of the two samples of carbonate filler particles was:

	Ground Carbonate	Granular Carbonate
On Tyler 14 (>1180 microns)	0	0
On Tyler 20 (>850 microns)	0	2
On Tyler 35 (>425 microns)	0	39
On Tyler 65 (>212 microns)	19	82
On Tyler 100 (>150 microns)	62	92
Weight fraction < 150 microns	38%	8%

The two finished products were then tested for bulk density and for their ability to dispense from a washing machine drawer of the shower type. A Zanussi (Trade Mark) dispenser was used. 150g of the test product were placed in the drawer with water flowing at 3 l/min at 20°C for 2 minutes. The weight of the residue left after the test is expressed as a percentage of the initial 150g. In this stressed test, it is considered that a product with residues below 30% is of good dispensing quality.

	Bulk Density (g/l)	Dispensing Residue(%)
Finished Product with ground carbonate filler particles	809	28
Finished Product with granulated carbonate filler particles (comparative)	780	17

In this example the use of the ground carbonate as a filler particle has increased the bulk density by 30 g/l. At the same time the dispensing performance remains good.

### Comparative Example 2

Another 40 kg of the base powder made in example 1 was taken and the coarse fraction sieved off. However, in this case, the fines fraction was not removed. This resulted in the base powder consisting of surfactant containing particles, containing 15% by weight with a particle size of less than 150 microns, and 31% by weight with a particle size of less than 212 microns.

Two finished products were made and tested according to the same series of steps in example 1, with the following results.

	Bulk Density (g/l)	Dispensing Residue (%)
Finished Product with ground carbonate filler particles	795	63
Finished Product with granulated carbonate filler particles	790	59

In this example the increase in bulk density due to the ground filler particles is only 5 g/l, and in both cases the dispensing profile is poor.

### Claims

1. A process for the preparation of a compact granular detergent composition comprising one or more detergent active ingredients and comprising the steps of:
  - i) making a base powder in the form of a free-flowing powder having a bulk density of at least 600g/l and having less than 10% by weight of particles less than 150 microns and less than 10% by weight of particles greater than 1700 microns.
  - ii) post-addition of additional ingredients,
 characterised in that said additional ingredients comprise filler particles at a level of from 5% to 20% by weight of the finished product, and that at least 20% by weight of the filler particles is either less than 150 microns, or greater than 1180 microns.

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2. A process according to claim 1 characterised in that at least 40% by weight of the filler particles is either less than 150 microns, or greater than 1180 microns.
3. A process according to either claim 1 or 2 in which the filler particles are sodium, potassium or magnesium salts of citrates, sulphates, carbonates, bicarbonates or silicates, or a mixture thereof.
4. A process according either claim 1 or 2 in which the filler particles are either sodium citrate, layered sodium silicate, sodium bicarbonate, or a mixture of these.
5. A process according to any of the preceding claims in which the filler 40% by weight of the filler particles are less than 150 microns and in which the average particle size of the filler particles is not less than 50 microns.
6. A process according to any of the preceding claims characterised in that less than 10% by weight of the base powder is less than 212 microns.
7. A process according to any of the preceding claims characterised in that the finished detergent comprises less than 30% by weight of a blown powder.
8. A process according to any of the preceding claims characterised in that any blown powder comprises less than 10% of an anionic surfactant.
9. A free-flowing granular detergent composition having a bulk density greater than 650 g/l and comprising
  - i) from 5% to 25% by weight of anionic surfactant
  - ii) from 5% to 30% by weight of aluminosilicate builder
  - iii) from 5% to 20% by weight of filler particles comprising sodium, potassium or magnesium salts of citrates, sulphates, carbonates or silicates, or a mixture thereof characterised in that at least 20% by weight of the filler particles is either less than 150 microns, or greater than 1180 microns.
10. A composition according to claim 9 in which the filler particles are either sodium citrate, or layered sodium silicate, or a mixture of these.
11. A composition according to claim 9 or 10 characterised in that at least 80% by weight of the total amount of anionic surfactant present in the composition is in the fraction that passes through a Tyler sieve mesh 14, but does not pass through a Tyler Sieve mesh 65.



European Patent  
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# EUROPEAN SEARCH REPORT

Application Number

EP 92 20 2169

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
D,A	EP-A-0 270 240 (UNILEVER) * page 5, line 32 - line 52; examples * ---	1-11	C11D3/12 C11D17/06
D,A	EP-A-0 219 328 (UNILEVER) * page 4, line 36 - line 58; examples * ---	1-11	
A	EP-A-0 466 484 (UNILEVER) * page 3, line 29 - line 33 * ---	1-11	
A	GB-A-2 005 715 (COLGATE-PALMOLIVE) ---		
A	RESEARCH DISCLOSURE no. 312, April 1990, HAVANT GB pages 357 - 359, XP000104695 'Detergent powder production.' -----		
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. CL.5)
			C11D
Place of search	Date of completion of the search	Examiner	
THE HAGUE	12 MARCH 1993	DELZANT J-F.	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : number of the same patent family, corresponding document	

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